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(54) Acidic aqueous liquid compositions

(57) The invention relates to acidic aqueous compositions comprising sulphuric acid, a chelating agent having a pKa not higher than 4, and at least 0.1% by weight of the total composition of a surfactant,. Preferred compositions therein further comprise a source of active oxygen, or mixtures thereof, and/or a thickening surfactant system such as a quaternary ammonium compound together with a short chain amine oxide. Said compositions are particularly suitable for the cleaning of toilet bowls providing thereby improved surface appearance to the surface cleaned.

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Description

Technical field

The present invention relates to acidic aqueous liquid compositions, more particularly to acidic aqueous compositions comprising sulphuric acid and a specific cheating agent, or mixtures thereof. Said compositions find particular application in the cleaning of hard-surfaces, especially inclined hard-surfaces, such as toilet bowls and the like.

Background

On hard surfaces there is often deposition of mineral encrustations. This type of soil is composed of calcium carbonate and, in case of toilet bowls, of other calcium salts. The deposition of mineral encrustations is related to water evaporation and to the action of microorganisms (e.g., bacteria) present on toilet bowl surfaces. Mineral encrustations are aesthetically unpleasant and, especially in toilet bowls, favor the subsequent deposition of additional soils. It is therefore important to inhibit/reduce this soil deposition phenomenon.

A great variety of acidic compositions have been described in the art. Acidic compositions comprising a strong source of acidity, such as sulphuric acid, are particularly interesting for the cleaning of hard-surfaces, especially for the hygienic cleaning of sanitary fittings such as toilet bowls and the like.

However, such compositions containing sulfuric acid have not been found to be satisfactory from a consumer viewpoint regarding the surface appearance, i.e. shine and/or cleaning performance, delivered to the surface being treated therewith. Indeed, an acidic composition containing sulphuric acid, when used to remove mineral encrustations from a hard-surface, may leave residues on it, which appear as streaks when water has evaporated. This is particularly evident when the encrustations are enriched of calcium salts, for instance, in presence of hard water and when the composition is used neat. In other words, it has been found that the presence of sulfate anions coming from sulphuric acid and of calcium cations coming from mineral encrustations and/or from the hardness of the tap water used, react together so as to form calcium sulfate residues (as depicted in the following reactions) which are detrimental to the final surface appearance.

$$2H^+ + SO4^{2-} + CaCO_{3(encrustation)} \rightarrow H_2O + CaSO_4 + CO_{2(gas)}$$

$$2H^+ + SO4^{2-} + Ca^{2+}_{(from\ tap\ water)} \rightarrow 2H^+ + CaSO_4$$

In fact, calcium sulfate residues may make the consumer believe that the acidic composition is not effective in removing the toilet soils because the calcium sulfate residues can be perceived by the consumer as soils not having been removed. In addition or alternatively, consumer may think that product performance in terms of shine is not satisfactory because of calcium sulfate residues. Also, calcium sulfate residues may slightly decrease the mineral encrustation removal effectiveness of the acidic composition. In fact, calcium sulfate residues cover the mineral encrustations thus lowering the collision probability between H+ ions and mineral encrustations themselves. This reduces the probability that said encrustations could react with H+ ions and consequently be removed.

It is thus an object of the present invention to formulate acidic aqueous compositions comprising sulphuric acid, which enable to remove mineral encrustations from hard surfaces without leaving residues thus delivering improved surface appearance.

It is also desirable to formulate compositions which comprise beaches. Indeed, beaches possess many desirable properties, including disinfection properties. Furthermore, such compounds, as monopersulfuric acid, are particularly effective as disinfectants and in removing and or decolouring stains for household cleaning applications. However, when formulating acidic aqueous compositions which further comprise bleaches stability problems appear, i.e. in general beaches raise compatibility issues in relation with the acids used to remove mineral encrustations. It is thus an object of the present invention to provide an acidic aqueous composition which can be formulated with beaches, in particularly persulfuric acid, in a stable manner.

It has now been found that the above mentioned objects could be met by formulating an acidic aqueous composition comprising sulphuric acid and a cheating agent having a pKa not higher than 4, preferably not higher than 2. More particularly, it has unexpectedly been found that the addition of such a chelating agent to an acidic aqueous composition comprising sulphuric acid allows to inhibit the formation and subsequent precipitation of calcium sulfate, when the above composition is applied on inorganic soils like calcium carbonate or calcium phosphate encrustations commonly found in hard-surfaces, like toilet bowls, resulting thereby in improved surface appearance.

An advantage of the present invention is that the end result advantage in terms of surface appearance is particularly noticeable when the composition is used neat, for example, when used for cleaning toilet bowls above the toilet water line, when the water hardness is high and in presence of calcium salts enriched soils.

Another advantage of the present invention is that said aqueous acidic compositions are efficient on various surfaces to clean various soils and stains.

Additionally, the preferred compositions of the present invention which further comprise a source of active oxygen, such as monopersulfuric acid, when used to treat hard surfaces, especially toilet bowls, exhibit outstanding soil discoloration together with a germicidal action, this when used both neat or diluted. A further advantage of the compositions of the present invention is that said compositions are chemically stable for long storage periods. Indeed, the chelating agents having a pka not higher than 4 contribute to the stability of the acidic aqueous compositions of the present invention which further comprise a source of active oxygen.

Also, the preferred compositions of the present invention which further comprise a thickening surfactant system comprising quaternary ammonium compound and short chain amine oxide (C6-C10), exhibit improved thickening properties at low total thickening surfactant level.

The following patent applications are representative of the prior art.

EP-A-421 974 discloses aqueous compositions of peracetic acid which further comprise a sequestrant such as hydroxyaminocarboxylic acids, alkyl polyphosphonic acid/ alkyl phosphonic acid derivatives. No sulfuric acid is disclosed in EP-A-421 974.

EP-A-411 708 discloses acidic hard surface cleaners having a pH of from 1 to 4 and comprising amongst other ingredients, a synthetic organic detergent, an organic acid, an aminoalkylenephosphonic acid and phosphoric acid. No sulphuric acid is disclosed in EP-A-411 708.

EP-B-047 150 discloses aminomethylenephosphonic acid solutions containing at least 10% by weight of the total solution of active phosphonic acid, i.e. aminomethylenephosphonic acid and acids such as sulphuric acid, as a non-oxidizing mineral acid. No surfactants are disclosed in EP-B-047 150.

EP-A-346 667 discloses stabilized aqueous mixed permonosulphuric acid/sulphuric acid solutions containing a sequestrant such as a phosphorus-containing compound, commercially available from Monsanto under the trade name Dequest, in an amount of from 0.01% to 1% by weight and a stabilizing quantity of an added metal compound. The solutions of EP-A-346 667 are suitable for use to strip photoresist residues from semiconductor surfaces. The solution of permonosulphuric acid may be produced by reacting sulphuric acid and hydrogen peroxide. EP-A-346 667 further discloses that surfactants may be added and that a suitable quantity is from 20 to 500 ppm by weight of the solution.

J 06340617, (Derwent abstract), discloses safe peracetic acid compositions comprising peracetic acid, hydrogen peroxide, acetic acid, a stabilizer such a pyrophosphonic acid or diethylene triamine penta methylenephosphonic acid, and sulphuric acid. An example is disclosed with 0.2% by weight of sulphuric acid and 0.2% by weight of 1-hydroxyethylidene-1,1-diphosphonic acid. No surfactants are disclosed.

Summary of the invention

The present invention encompasses an acidic aqueous composition comprising sulphuric acid, a chelating agent having a pKa not higher than 4 and at least 0.1% by weight of the total composition of a surfactant.

In a preferred embodiment the acidic aqueous compositions of the present invention further comprise a thickening surfactant system comprising a quaternary ammonium compound and a short chain amine oxide. In a preferred embodiment, the acidic aqueous compositions of the present invention further comprise a source of active oxygen, or mixtures thereof.

The present invention also encompasses a process of treating a hard-surface, especially toilet bowls, wherein an acidic aqueous composition comprising sulphuric acid and a chelating agent having a pKa not higher than 4, is contacted to said surface, thereby delivering improved surface appearance to said surface.

Detailed description of the invention

The compositions of the present invention are aqueous liquid compositions comprising, as a first essential ingredient, sulphuric acid.

Sulphuric acid suitable to be used herein is, for example, the one commercially available from MERCK.

The compositions of the present invention comprise from 0.1% to 20% by weight of the total composition of sulphuric acid, preferably from 0.2% to 15% and more preferably from 0.5% to 10%.

The compositions of the present invention are acidic. Accordingly, the compositions herein are formulated at a pH between 0 to 6, preferably at a pH between 0 and 4 and more preferably at a pH between 0 and 2. Acidity further contributes to formulate compositions according to the present invention which exhibit good mineral encrustations removal performance while having also good disinfecting properties. The compositions of the present invention apart from sulphuric acid may further comprise other organic and/or inorganic acids. Particularly suitable organic acids to be used herein are aryl and/or alkyl sulfonate, such as methane sulfonic acids, succinic acid and the like. Particularly suitable inorganic acids are further phosphoric acid, nitric acid and the like.

The compositions of the present invention are aqueous liquid compositions comprising, as a second essential ingredient, a chelating agent having a pKa being not higher than 4, or mixtures thereof, preferably having a pKa being not higher than 2.

The chelating agents to be used according to the present invention should have a pKa not higher than 4, preferably not higher than 2, so that they are not totally protonated in the compositions of the present invention which are formulated at very low pH values. In other words, the chelating agents of the present invention are negatively charged at very low pH value, for instance, at pH 1 and thus contribute to inhibit the formation and subsequent precipitation of poorly water soluble calcium salts such as calcium sulfate.

Below is showed the mechanism of action of chelating agents according to the present invention when applied in a very acidic composition:

$$2H^+ + SO4^{2-} + Ca^{2+} + CaCO_3 + Chelant \rightarrow H_2O + Ca^{2+}SO4^{2-} + CO_2 + (Chelant)^{M-}\ Ca^{2+}$$

pH = 0.5 - Chelating agent is protonated
locally pH > 1 - Chelating agent is partially unprotonated

Protons of sulfuric acid are able to dissolve calcium carbonate crystals thus liberating Ca++ and CO3-- ions into the composition in contact with the surface of, for instance, a toilet bowl to be treated. The CO2 release plus the water formation as indicated in the above reaction contribute to increase the local pH from about 0.5 to about 1 where the chelating agents of the present invention having a pKa not higher than 4 become partially unprotonated and therefore inhibit/reduce calcium sulfate precipitation by binding Ca++ in soluble complexes. Also, they could bind Ca++ ions of the encrustation itself, thus helping its removal.

Suitable chelating agents having a pKa being not higher than 4 are phosphonate-based chelants having a number of phosphonate groups ranging from 1 to 6 and being preferably selected from the following group; or mixtures thereof :

1) amino poly alkyl phosphonic acids with the following formula:

$$[NX_2]_{a1} - [(CH_2)_nNX_m]_{a2} - [(CH_2)_2\ NX_2]_{a3}$$

where:

X = Methylene Phosphonic Acid ($CH_2H_2PO_3$)
n = 0 to 1
m = 1 to 3
a1 = 0 to 1
a2 = 1 to 4
a3 = 0 to 1

2) metaphosphoric acid $(HPO_3)_n$

3) pyrophosphoric acid ($H_4P_2O_7$).

4) methylidene di phosphonic acid $CH_2(H_2PO_3)_2$

Suitable amino poly alkyl phosphonic acids are diethylenetriamine penta methylene phosphonic acid, commercially available from Monsanto under the trade name Dequest ® 2066A; amino trimethylene phosphonic acid commercially available from Albright&Wilson under the trade name Briquest ® 301-50A; tetraethylene pentaamine hepta methylene phosphonic acid commercially available from Albright&Wilson under the trade name Briquest ® 785; pentaethylene hexaamine octa methylene phosphonic acid commercially available from Albright&Wilson under the trade name Briquest ® 8106.

Preferred amino poly alkyl phosphonic acid to be used herein is diethylenetriamine penta methylene phosphonic acid.

Metaphosphoric acid suitable to be used herein may be the one commercially available from Carlo Erba.

Pyrophosphoric acid suitable to be used herein may be the one commercially available from Carlo Erba.

The compositions of the present invention comprise from 0.05% to 3% by weight of the total composition of a chelating agent having a pKa not higher than 4, or mixtures thereof, preferably from 0.05% to 2% by weight and more preferably from 0.05% to 1%.

The compositions of the present invention are aqueous liquid compositions comprising at least 0.1% by weight of the total composition of a surfactant, or mixtures thereof. The compositions of the present invention comprise sur-

factants to provide further cleaning benefits. Also, surfactant systems can be used to provide viscosity to the compositions herein, and that is desirable since the compositions herein are likely to be used on inclined surfaces such as bath tubs, sinks or toilet bowls. Thickened compositions have a better cling onto inclined surfaces, thus a longer residence time for the composition to remove mineral encrustations.

Thus the surfactants of the present invention may be any surfactant selected from the group of anionic, nonionic, zwitterionic and cationic surfactants in amounts ranging up to 50% by weight of the total composition, preferably from 0.1% to 30% and more preferably from 0.1% to 10%.

Suitable anionic surfactants include alkyl or alkylene sulfate or sulfonates, alkyl or alkylene ether sulfates or sulfonates, linear alkyl benzene sulfonate and the like. Suitable cationic surfactants include quaternary ammonium salts. Suitable nonionic surfactants for use herein include ethoxylated carboxylic acids, amine oxides and alcohol ethoxylates. Emulsions of nonionic surfactants, such as in co-pending European patent application EP 598 692, are also suitable to provide pseudoplastic and thixotropic compositions, which allow excellent spreading and clinging characteristics on dry surfaces.

A suitable thickening surfactant system highly preferred herein that leads to excellent spreading and clinging on wet surface is constituted by mixtures of a quaternary ammonium compound, or mixtures thereof, together with a short chain amine oxide, or mixtures thereof. Said compositions are Newtonian. By "Newtonian" it is meant herein a composition which has the same viscosity within a very wide range of applied shear stresses.

Suitable quaternary ammonium compounds to be used herein are quaternary ammonium compounds wherein one or two of the hydrocarbon groups linked to nitrogen are a linear or branched alkyl group of 6 to 30 carbon atoms, preferably of 10 to 25 carbon atoms and more preferably 12 to 20 carbon atoms, saturated or unsaturated, and wherein the other hydrocarbon groups (i.e. three when one hydrocarbon group is a long chain hydrocarbon group as mentioned hereinbefore or two when two hydrocarbon groups are long chain hydrocarbon groups as mentioned hereinbefore) linked to the nitrogen are independently substituted or unsubstituted, linear or branched, alkyl chain of from 1 to 4 carbon atoms, preferably of from 1 to 3 carbon atoms and more preferably are methyl groups. In the embodiment of the present invention where as sources of active oxygen, persulfate salts or mixtures thereof, are used the quaternary ammonium compound is preferably a non-chloride quaternary ammonium compound. The counterion used in said quaternary ammonium compounds are compatible with any source of active oxygen if present and are selected from the group of fluoride or methyl sulfate, or methylsulfonate, or hydroxide and the like. Particularly preferred to be used herein are trimethyl quaternary ammonium compounds like myristyl trimethyl ammonium methylsulfate, cetyl trimethyl ammonium methylsulfate and/or tallow trimethyl ammonium methylsulfate. Such trimethyl quaternary ammonium compounds are commercially available from Hoechst, or from Albright & Wilson under the trade name EMPIGEN CM®.

The compositions according to the present invention comprise up to 20% by weight of a quaternary ammonium compound, or mixtures thereof, preferably of from 0.1% to 15%, more preferably of from 0.1% to 10% and most preferably of from 1% to 5%.

Suitable short chain amine oxides to be used herein are amine oxides having the following formula $R_1R_2R_3NO$ wherein R1 is a C6 to C10 alkyl group, preferably a C8 to C10 alkyl group and wherein R2 and R3 are independently substituted or unsubstituted, linear or branched alkyl groups of from 1 to 4 carbon atoms, preferably of from 1 to 3 carbon atoms and more preferably are methyl groups. R1 may be a linear or branched alkyl group, being saturated or unsaturated. Suitable short chain amine oxides for use herein are preferably compatible with any source of active oxygen if present. Preferred short chain amine oxides for use herein are for instance natural blend C8/C10 amine oxide available from Hoechst.

The compositions according to the present invention comprise up to 15% by weight of a short chain amine oxide, or mixtures thereof, preferably of from 0.1 % to 10% more preferably of from 0.1 % to 5% and most preferably of from 0.1% to 3%.

The total level of thickening surfactant system, i.e. of quaternary ammonium compound and of short chain amine oxide, to be used in a given aqueous acidic composition of the present invention depends on the thickening desired for said composition, said level being up to 20%, preferably between 1% and 15%, and more preferably between 1% and 6%. Suitable weight ratios of said short chain amine oxide to said quaternary ammonium compound range from 1:2 to 1:100, preferably from 1:4 to 1:30 and more preferably from 1:10 to 1:20. Desired viscosity herein ranges from 150 cps and up at 20°C, preferably of from 250 cps to 1500 cps and more preferably of from 250 cps to 900 cps, when measured with a Brookfield viscometer at 60 rpm with a spindle n° 2 or with the Carri-med rheometer at 50 dyne/cm2.

In a preferred embodiment the compositions of the present invention may comprises a source of active oxygen, or mixtures thereof, which is an acid-stable bleach. By "acid-stable" it is meant herein a compound which is stable in the acidic environment of the compositions herein. By stable, it is meant herein that a composition of the present invention further comprising a source of active oxygen, or mixtures thereof, such as persulfate salt, preferably does not undergo more than 50% persulfate loss, in six months at room temperature (20°C-25°C). Persulfate concentration can be measured by titration with potassium permanganate after reduction with a solution containing ammonium ferrous sulphate. Said stability test method is well known in the art and is reported, for example, on the technical information sheet of Curox® commercially available from Interox. Alternatively persulfate concentration can also be measured using a chro-

cidal action.

The compositions according to the present invention may comprise up to 30% by weight of the total composition of said source of active oxygen, or mixtures thereof, preferably from 0.1% to 30%, more preferably from 0.1% to 20%, and most preferably from 0.1% to 15%.

The compositions according to the present invention are aqueous. The compositions according to the present invention comprise from 40% to 99% by weight of the total composition of water, preferably from 60% to 95%, most preferably from 70% to 90%. Deionized water is preferably used.

Depending on the end use envisioned, the compositions according to the present invention may further comprise a variety of other ingredients including organic or inorganic alkalis, dyes, optical brighteners, builders, other chelants, pigments, colorants, enzymes, dye transfer inhibitors, solvents, buffering agents, stabilizers, perfumes and the like.

The present invention further encompasses a process of treating a hard-surface wherein an acidic composition comprising sulphuric acid and a chelating agent having a pKa being not higher than 4, is contacted to said surface, thereby delivering improved surface appearance to said surface.

By " improved surface appearance to said surface" it is meant herein that the shine, and/or cleaning performance, i.e. mineral encrustation removal performance, delivered to the surface treated with the compositions of the present invention is improved. In other words, it has been found that the shine and/or cleaning performance delivered to the hard-surfaces treated with a composition of the present invention comprising sulphuric acid and a chelating agent having a pKa not higher than 4, is improved as compared to the shine and/or cleaning performance delivered when treating said hard-surfaces with the same composition but without any such chelating agent.

Actually, the present invention is based on the finding that the effectiveness of the compositions of the present invention on mineral encrustations, is increased as compared to the same composition without any such chelating agent.

Any of the compositions already mentioned herein before may be used in the process of treating hard-surfaces according to the present invention.

In the process of the present invention said composition may be used neat or in its diluted form. By "in its diluted form" it is meant herein that said compositions may be diluted with water up to 99% of water. Said dilution may occur either before, after or while said composition is applied to a hard-surface.

The compositions herein find a preferred application in the cleaning of toilet bowls and bath tubs. While cleaning toilet bowls compositions according to the present invention may be diluted while or after they are applied to the surface to be cleaned. For example, said compositions may be dispensed from a container onto said hard-surface, then diluted in water and left to act onto said surfaces, then removed by rinsing or flushing.

As used in the foregoing paragraphs, the expression "treating" includes mineral encrustations removal as the composition used in the process according to the present invention comprises sulphuric acid, washing as the compositions used in the process according to the present invention may further comprise surfactants and/or bleaching as said compositions may also comprise a source of active oxygen, preferably persulfate salts.

The present invention is further illustrated by the following examples.

Examples

Compositions are made which comprise the listed ingredients in the listed proportions (weight %).

Compositions (% by weight)	#1	#2	#3	#4	#5
Sulphuric acid	6	6	6	6	6
Curox®	6	6	6	6	6
C16 trimethyl ammonium methylsulfate	4	4	4	4	4
C8/C10 amine oxides	0.2	0.2	0.2	0.2	0.2
Diethylene triamine penta (methylene phosphonic acid)	--	0.1	--	--	--
Amino trimethylene phosphonic acid	--	--	0.1	--	--
Metaphosphoric acid	--	--	--	0.1	--
Pyrophosphoric acid	--	--	--	--	0.1
Water and minors	up to 100				
pH	0.5	0.5	0.5	0.5	0.5
viscosity (m Pa s)	300	300	300	300	300

* Curox® is one of the commercial names of monopersulfate salts.

Compositions #2, #3, #4 and #5 are representative of the present invention. They are acidic aqueous compositions comprising sulphuric acid, surfactants and a chelating agent having a pKa being not higher than 4. Composition #1 is taken as a reference, it is free of chelating agent having a pKa being not higher than 4.

A)

The above compositions were evaluated for their surface appearance, i.e. cleaning and shine performance, on white ceramic tiles soiled with typical toilet mineral encrustations. The ceramic tiles were soaked for 2 minutes in the different compositions mentioned herein before (neat conditions). Then the tiles were rinsed and dried.

To evaluate the performance of the compositions, a sets of spectophotometric measurements were made. This analysis can be meant as a technical measure of surface appearance. In fact, reflectance spectra (L value) was measured on soiled tiles (A), on tiles after products application (B) and on completely shiny/cleaned tiles (C). The measure of composition performance (index) was calculated using the following formula:

$$\frac{L(B)-L(A)}{L(C)-L(A)} \times 100$$

The results were as following:

Compositions	#1	#2	#3	#4	#5
Index	62	95	89	87	80

The index represents the measure of tile surface appearance after product application. Index 0 means completely soiled tile, whilst index 100 means completely shiny/cleaned tile.

Accordingly, it has been observed that the compositions of the present invention (compositions #2, #3, #4 and #5) exhibit improved cleaning performance and improved shine, as compared to composition #1 which is free of a chelating agent having a pKa being not higher than 4.

B)

Above compositions #1 and #2 were further evaluated to compare the residues (i.e., calcium sulfate) left after application on black ceramic tiles soiled with calcium carbonate only. Said compositions were poured on these inclined ceramic tiles and let act for 3 minutes (neat conditions). Then the tiles were rinsed and dried.

To evaluate the performance of the compositions, a sets of visual gradings were made. This analysis can be meant as a measure of product residuality on surfaces from a consumer standpoint.

The results were as following:

Compositions	#1	#2
Residues left index*	100	65

* index 100 is assumed as reference value

Accordingly, it has been observed that the composition of the present invention (composition #2) exhibits a much lower residuality as compared to composition #1 which is free of a chelating agent having a pKa being not higher than 4. Indeed less calcium sulfate residues were left on the surfaces treated with the composition of the present invention.

Also the compositions of the present invention (compositions #2, #3, #4 and #5) were found to be stable over long periods of time. Indeed, these compositions had not more than 10% loss after 1 month at room temperature.

Claims

1. An acidic aqueous composition comprising sulphuric acid, a chelating agent having a pKa being not higher than 4 and at least 0.1% by weight of the total composition of a surfactant.

2. A process of treating hard-surface wherein an acidic aqueous composition comprising sulphuric acid and a chelating agent having a pKa being not higher than 4, is contacted to said surface.

3. A composition or process according to any of the preceding claims wherein said composition comprises from 0.1% to 20% by weight of the total composition of said sulphuric acid, preferably from 0.2% to 15% and more preferably from 0.5% to 10%.

4. A composition or process according to any of the preceding claims wherein said composition comprises from 0.05% to 3% by weight of the total composition of said cheating agent having a pKa being not higher than 4, preferably not higher than 2, or mixtures thereof, preferably from 0.05% to 2% and more preferably from 0.05% to 1%.

5. A composition or process according to any of the preceding claims wherein said chelating agent is a phosphonate-based chelant having from 1 to 6 phosphonate groups and being preferably selected from the following group or mixtures thereof:

   1) amino poly alkyl phosphonic acids with the following formula:

   $$[NX_2]_{a1} - [(CH_2)_nNX_m]_{a2} - [(CH_2)_2 NX_2]_{a3}$$

   where:

   X = Methylene Phosphonic Acid ($CH_2H_2PO_3$)
   n = 0 to 1
   m = 1 to 3
   a1 = 0 to 1
   a2 = 1 to 4
   a3 = 0 to 1

   2) metaphosphoric acid,

   3) pyrophosphoric acid.

   4) methylidene di phosphonic acid

6. A composition or process according to any of the preceding claims wherein said chelating agent is diethylenetriamine penta methylene phosphonic acid, amino trimethylene phosphonic acid, tetraethylene pentaamine hepta methylene phosphonic acid, pentaethylene hexaamine octa methylene phosphonic acid, pyrophosphoric acid, metaphosphoric acid, methylidene di phosphonic acid or mixtures thereof, and preferably diethylenetriamine penta methylene phosphonic acid.

7. A composition or process according to any of the preceding claims wherein said composition has a pH of from 0 to 6, preferably of from 0 to 4 and more preferably of from 0 to 2.

8. A composition or process according to any of the preceding claims wherein said composition further comprises a source of active oxygen, or mixtures thereof, preferably a persulfate salt, more preferably monopersulfate, and said composition comprising up to 30% by weight of the total composition of said source of active oxygen, or mixtures thereof, preferably from 0.1 % to 30%, more preferably from 0.1% to 20% and most preferably at a level of from 0.1% to 15%.

9. A composition or process according to any of the preceding claims wherein said composition comprises up to 50% by weight of the total composition of a surfactant, or mixtures thereof, preferably a thickening surfactant system comprising a quaternary ammonium compound or mixtures thereof, and an amine oxide having the following formula $R_1R_2R_3NO$ wherein R_2 and R_3 are independently C1-C4 alkyl groups, preferably alkyl groups of from 1 to 3 carbon atoms, and more preferably are methyl groups, and wherein R_1 is a C6 to C10 alkyl group, preferably a C8 to C10 alkyl group or mixtures thereof.

10. A composition or process according to claim 9 wherein said quaternary ammonium compound is a quaternary ammonium compound wherein one or two of the hydrocarbon groups linked to nitrogen are a linear or branched alkyl group of 6 to 30 carbon atoms, preferably of 10 to 25 carbon atoms and more preferably of 12 to 20 carbon atoms, saturated or unsaturated, and wherein the other hydrocarbon groups linked to the nitrogen are independently substituted or unsubstituted, linear or branched alkyl chain of from 1 to 4 carbon atoms, preferably of from 1 to 3 carbon atoms and more preferably are methyl groups and wherein the counterion used in said quaternary ammonium compound is preferably selected from the group of fluoride, or methyl sulfate, or methylsulfonate or hydroxide.

11. A composition or process according to any of the preceding claims 9 or 10 wherein in said composition the weight ratio of said amine oxide to said quaternary ammonium compound is from 1:2 to 1:100, preferably from 1:4 to 1:30 and more preferably from 1:10 to 1:20, and wherein the total level of said thickening surfactant system is no more than 20%, preferably between 1% to 15%, more preferably between 1% to 10% and most preferably between 1% to 6%.

12. A process according to any of the claims 2 to 11 wherein said hard-surface is a toilet bowl.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 87 0051

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 276 774 (MICRO-IMAGE TECHNOLOGY LIMITED) * page 3, line 44 - line 58 * * page 4, line 8 - line 17 * * claims 1-6,10,15 *	1-8	C11D3/39 C11D3/36
X	EP-A-0 560 324 (MITSUBISHI GAS CHEMICAL CO) * page 4, line 5 * * page 5, line 7 - line 13 * * claims 1,5,6,10-13 *	1,2,4-8	
D,Y	EP-A-0 188 025 (UNILEVER NV ET AL.) * column 2, line 19 - line 23 * * column 2, line 60 - line 65 * * column 3, line 1 - line 48 * * column 4, line 39 - line 66 * * claims *	1	
Y	FR-A-1 453 022 (CALGON CORPORATION) * page 2, right column, line 20 - line 21 * * page 3; table 1 * * page 4; table 3 * * claims *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C11D
A D	EP-A-0 598 694 (PROCTER & GAMBLE CO.) * the whole document * & EP-A-0 598 692	1-12	
A	GB-A-2 071 688 (JEYES LIMITED) * page 1, line 14 - line 31 *	1,9-11	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	16 October 1995	Pelli Wablat, B

EPO FORM 1503 03.82 (P04C01)

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document